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PRESENT STATUS SULFEROX® PROCESS

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Sulfur Recovery Conference
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San Antonio, Texas

®SulFerox is a registered service mark of Shell Oil Company
Shell Global Solutions is a trading style used by a network of
technology companies of the Royal Dutch/Shell Group

PRESENT STATUS SULFEROX PROCESS

Cornelis J. Smit¹ and Eva C. Heyman²

ABSTRACT

The licensing of the SulFerox process has changed since early 1998. SulFerox is licensed by Shell International Oil Products B.V. and by the authorised licensors of the process Le Gaz Integral in Nanterre, France and Westfield Engineering & Services in Houston, Texas. SulFerox chemicals are still supplied by The Dow Chemical Company and support to operators in the form of solvent analysis is given. Other operational services are on offer from Shell Global Solutions³ and the authorised licensors.

The application of the SulFerox process is partly shifting from the traditional oil & gas industry to the abatement of H₂S from (syn)gas generated from the gasification of a range of feedstocks. Due to the range of impurities present in syngas other gas purification units may be required also and need to be integrated with the SulFerox process in the treating scheme.

Efforts to optimise current design and operation of SulFerox plants continue. Smooth steady operation of a SulFerox unit can be obtained by the automation of the addition of chemicals, coupled to the production of sulfur. Reduction in capital expenditure, particularly for small gas flows, was successfully demonstrated by a two vessel design.

Despite emerging new processes the SulFerox process remains competitive in certain applications, particularly for gas streams with an unfavourable H₂S/CO₂ ratio for scrubbing with a caustic solution.

Keywords: SulFerox, licensing, syngas, desulfurisation, optimisation, liquid redox

INTRODUCTION

SulFerox®⁴ is a redox-based process that converts H₂S in sour gas to elemental sulfur through reaction with aqueous ferric iron, Fe³⁺. Patented organic Ligands or chelating agents are used to increase the solubility of iron in the operating solution. As a result of the high iron concentration in the solution the rate of liquid circulation can be kept low and consequently the equipment is small. By reaction with H₂S the Fe³⁺ is reduced to Fe²⁺ and needs to be oxidised back to Fe³⁺. This is accomplished by reaction with air in a separate regeneration vessel.

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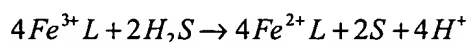
⁴ SulFerox is a registered service mark of Shell Oil Company

At the latest GRI conference (Oostwouder 1997) a SulFerox process update was given by The Dow Chemical Company with emphasis on new areas and new applications of the SulFerox process. For new applications a shift from the US to Europe and South East Asia and a shift from the oil industry to the “alternative energy industry” was foreseen.

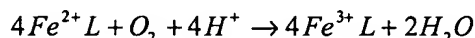
Since that time a number of changes in SulFerox licensing have occurred that will also be addressed in this contribution, together with the aspects mentioned above.

Process Chemistry

The process chemistry of the SulFerox process is the basic Fe^{3+}/Fe^{2+} redox system and is well known and described previously (Fong 1987 and Wubs 1994). In the contactor H_2S reacts with Fe^{3+} according to:



The formed elemental sulfur is removed by filtration and the SulFerox solution is regenerated with air:



The key of the SulFerox technology is the ligand (denoted L) used in the process. The application of this ligand allows the use of relatively high total iron concentrations ($\geq 1\%$ w) in the optimal pH range for H_2S abatement.

During regeneration side reactions occur leading to degradation of the ligand(s) added to the SulFerox solution (Wubs 1993). The key to the successful operation of the SulFerox process is a proper control of this degradation rate and managing the continuous purge of degradation products and addition of fresh process chemicals to arrive at a steady state operation. A number of strategies are being employed to limit the rate of ligand degradation.

LICENSING SITUATION

Since the latest GRI conference a change has occurred in the licensing of the SulFerox process. In early 1998 The Dow Chemical Company announced that they went into an agreement with U.S. Filter to develop the next generation of iron redox technology. As a result Dow stopped all SulFerox licensing. Although not explicitly mentioned at that time the SulFerox process is still being licensed by Shell International Oil Products B.V.. Both Westfield Engineering & Services in Houston, Texas and Le Gaz Integral in Nanterre, France were appointed as authorised licensors for the process.

The Dow Chemical Company still supplies the SulFerox chemicals, solvent analyses and technical support. Further technical support can be obtained from Shell Global Solutions and the authorised licensors of the process.

PROCESS DEVELOPMENTS

Optimisation of chemicals addition

Process developments aim either at the reduction of capital cost or operating costs. As with most liquid redox processes chemicals costs are the major operating cost. The key to minimise chemicals consumption is the operation of the unit under steady state conditions. To achieve this optimisation of the chemicals addition rate is of prime importance, together with the optimisation of the amount of air that is supplied to the regenerator. For plants that run at a relatively stable feed gas rate and have a more or less constant hydrogen sulfide load this can be achieved by basing the chemicals addition rate on standard solution parameters as determined by solution sample analyses. Parameters that are of importance are the concentration of: iron; degradation by-product; primary ligand and the pH. In addition, the total salt load of the solution is important as expressed in the parameters viscosity, density and water content. For units that have both a varying feed rate and a hydrogen sulfide concentration that varies over time, operation under steady state conditions, using solution analyses only, is difficult. In a SulFerox unit near Lompoc, California a feed forward control system is in place. The unit is employed with an on-line H_2S analyser and the operator inputs the H_2S concentration into the process computer. From the reading of the inlet flow meter the computer continuously calculates the sulfur production. Based on the sulfur production the air requirement for the regenerator is calculated, together with the requirements for the individual chemicals. Subsequently, the computer adjusts the output of the air blowers and the chemicals additions pumps. Advantages of this way of control are:

1. More accurate addition of process chemicals giving;
 - a more steady state operation of the process solution;
 - a more reliable running of the plant;
 - a better control of the chemicals costs.
2. A controlled flow of air to the regenerator in accordance with the requirements for optimal regeneration of the solution.
3. Saving operator time from having to adjust the pump settings manually in the plant.

A similar system will be installed in a unit that is presently under construction.

Capital reduction

The standard lay-out of a SulFerox unit comprises a system with multiple vessels as is given in Figure 1. The sour gas enters the contactor where the hydrogen sulfide is oxidised to give elemental sulfur. The preferred and most versatile contactor is the sparged tower that can be used over a wide range of operating pressures. Within the design window the towers provide reliable and consistent treat, are easy to operate, have good turndown capabilities and require low solution circulation rates. This combination of properties makes the sparged tower the preferred contactor. Sparged tower contactors can be designed for co-current and counter current flow. Innovations in the sparged towers are mainly focused on the design of the gas spargers. Duckbill type rubber valve spargers pointing downwards have shown promising results. After the contactor the treated gas and SulFerox solution flow to the separator where gas and liquid are

separated. The sulfur laden solution is sent to the regenerator where Fe^{2+} is oxidised by a flow of air to give Fe^{3+} , thereby regenerating the solution. The now spent air, produced sulfur and regenerated solution go to the surge/settler tank and the sulfur is removed by filtration. Generally, only a fraction of the solution flows after thickening to the filter skid.

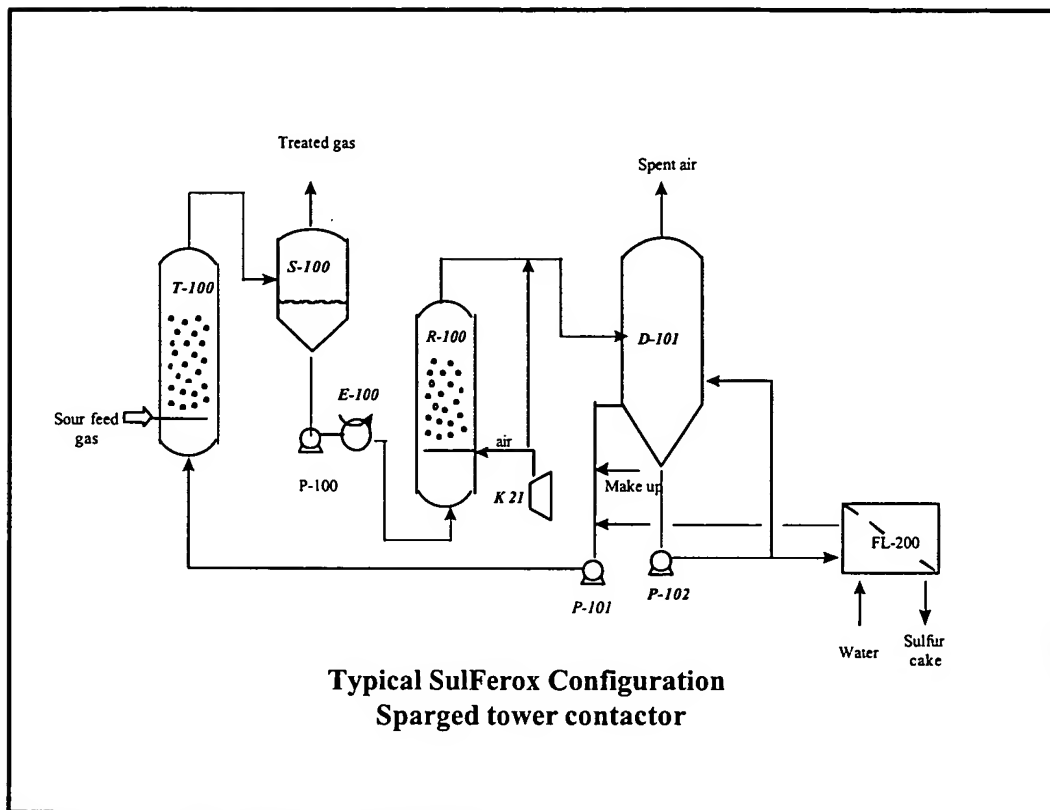


Figure 1 Lay out of the SulFerox process

For small gas flows and relatively low sulfur production rates a number of vessels can be combined. The sparged tower contactor T-100 can be combined with the separator S-100 and the regenerator R-100 can be combined with the surge vessel/thickener D-101. In order to keep the sulfur content in the solution low, a large proportion of the total flow can be directed to the filter FL-200. The Lompoc SulFerox unit has this configuration and is schematically shown in Figure 2.

Overall experience with this line up for the treating of amine treater off-gas at Lompoc is good. Inspection of the unit after an operational interval of nine months showed that hardly any plugging with sulfur had occurred in both vessels. Even the spargers of the vessels were mostly clear and only a few holes were blocked. The reason that this plant runs very satisfactorily can be attributed to the high quality of the operations, the almost full flow filtration keeping the sulfur content in the solution low and the optimal addition regime of the SulFerox chemicals. This result show that a two vessel design can be very effective and that good solution management can prevent effectively catastrophic blocking of vessels, piping and spargers.

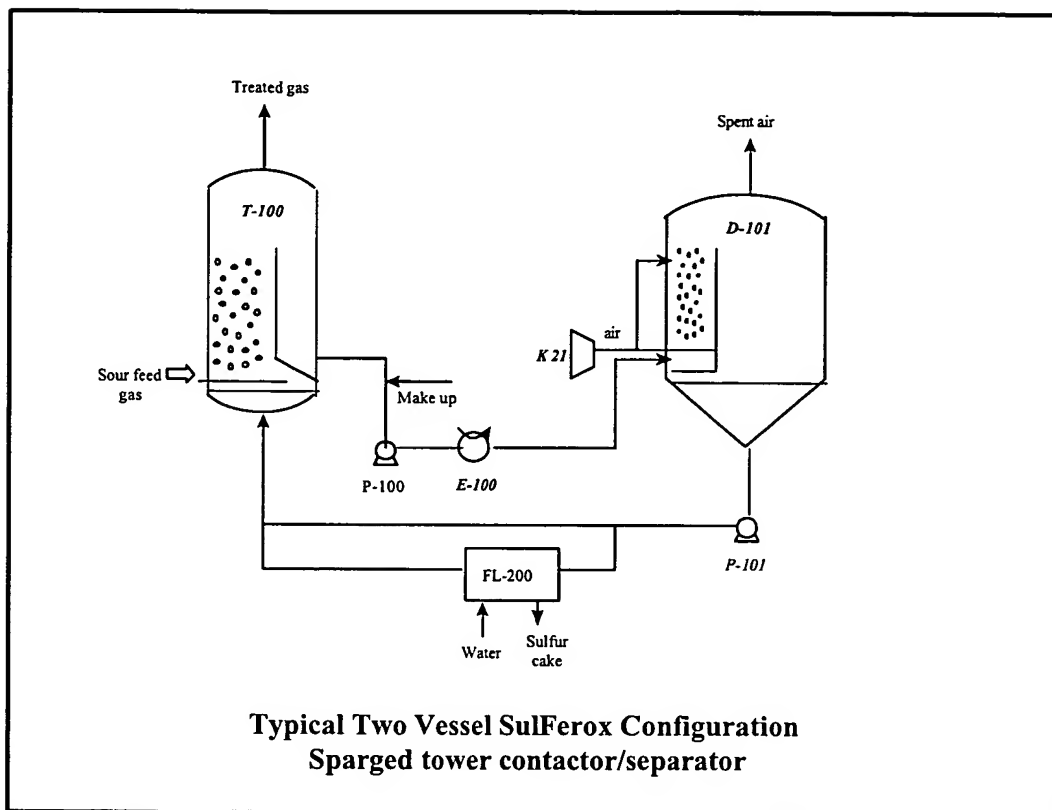


Figure 2 Two vessel design of the SulFerox process

Sparger developments

The key to the smooth operation of a liquid redox type of process is the efficient operation of the applied spargers. This holds for both the spargers in the contactor and for the air spargers in the regenerator. The function of the spargers is to evenly distribute the feed gas and the air into the SulFerox solution to achieve good mass transfer from the gas to the liquid phase. One of the major concerns in the use of spargers is blocking with sulfur particles. New sparger designs that show promise are the application of sleeved sparger elements in the regenerator and duckbill type rubber non return valves in the contactor.

SYNGAS TREATING

At the previous GRI Sulfur Recovery Conference it was predicted (Oostwouder 1997) that there would be a shift in the users of the SulFerox technology from the oil & gas industry in the US to other types of industry and to other areas in the world. Indeed this shift has materialised in the past two years and new applications are in the start-up phase or are under construction, particularly in Europe and Japan.

Of major interest in this case is the application of SulFerox technology in the removal of relatively small quantities of H_2S from processes that convert chemical or municipal waste into some type of

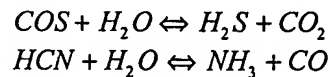
synthesis gas. These type of processes are developing under the various government supported programmes in Europe to convert waste into energy. All types of syngas have in common that they have a large concentration of CO and hydrogen. In addition the various types of syngas may contain high concentrations of HCN, NH₃ and COS (Baker 1991), depending on their origin (coal, oil residues, chemical waste, municipal waste). One of the major concerns was the potential formation of iron pentacarbonyl (Fe(CO)₅) by the reaction of CO with the iron in solution. Iron pentacarbonyl is a toxic compound that can lead to serious problems in downstream equipment depending on the use of the cleaned syngas (Golden 1991). Extensive laboratory tests were done using conditions and gas composition as given in Table 1 below.

Table 1 Syngas composition and tests conditions

Condition		remarks
Plant pressure psi (bar)	334 (23)	typical for coal gasification
Temperature °F (°C)	104 (40)	
Component	concentration (%V)	
carbon monoxide	60	CO/H ₂ ratio typical for coal gasification
hydrogen	30	
carbon dioxide	1.50	
hydrogen sulfide	0.30	
COS	0.03	in equilibrium with H ₂ S
nitrogen	balance	

The presence of Fe(CO)₅ was not observed in the treated syngas and moreover H₂S removal was very effective. Ligand degradation was found to be independent of the presence of syngas. In syngas the concentrations of H₂S and COS are in equilibrium and depend on the temperature, composition and pressure of the syngas. In the gasification of coal and oil residues under high pressures significant concentrations of COS will always be present.

As expected COS conversion in the SulFerox unit is low and consequently alternative COS removal is required to comply with the total sulfur recovery requirements. Depending on the source of the syngas the HCN content can be very high as well. High levels of HCN are undesirable because it can lead to the formation of thiocyanate and stable iron hexacyanoferrate complexes, leading to a higher chemicals consumption. Shell Global Solutions has developed technology (Van den Berg 1995) for the catalytic hydrolysis of both COS and HCN to give H₂S and NH₃, respectively:



In Figure 3 a potential syngas treating scheme is given. Feedstock is converted in a gasifier to obtain syngas. The produced syngas is cooled in a waste heat boiler and economiser and subsequently particulates are removed and the syngas is scrubbed. The thus obtained syngas is heated in a feed/effluent heat exchanger and further heated by a small steam heater.

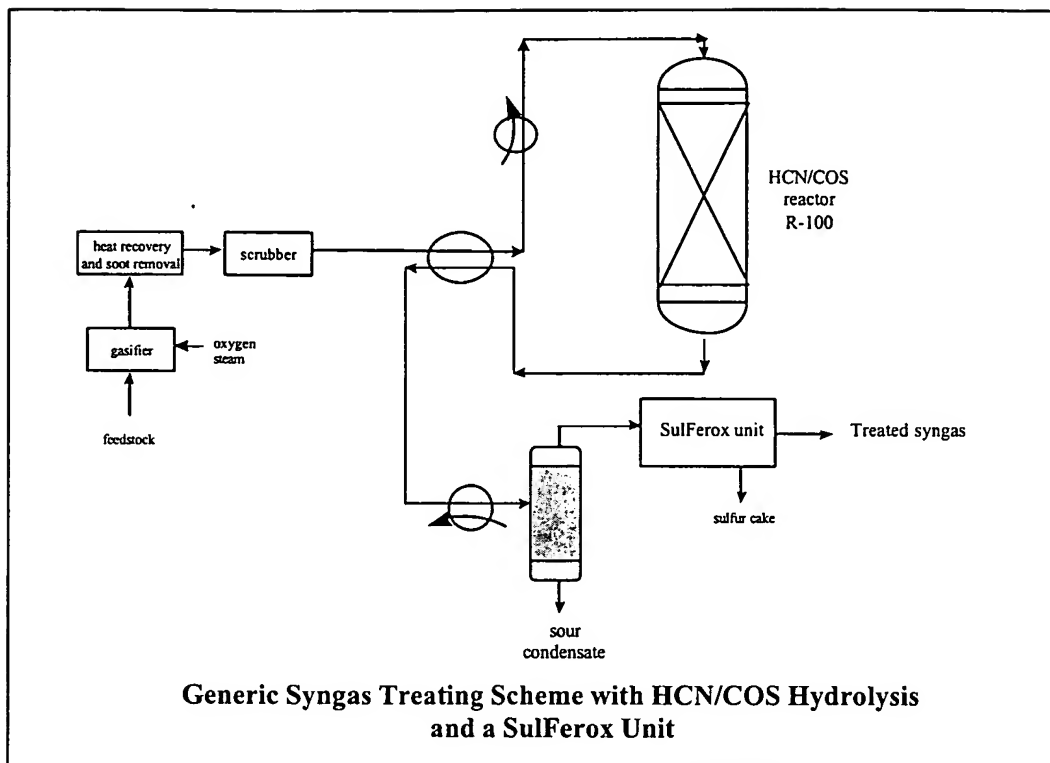


Figure 3 Syngas treatment scheme including a SulFerox unit

In the HCN/COS hydrolysis unit HCN can be removed to levels of down to ≤ 1 ppmV, whereas the final COS concentration is determined by a number of process conditions, however, levels of 6 - 10 ppmV can be obtained. Downstream of the hydrolysis reactor the syngas is cooled down and water -together with the formed ammonia- is removed in a gas liquid séparation step. The sour syngas obtained in this way is virtually free of solids, HCN and ammonia and is perfectly suited for H₂S removal using the SulFerox process.

Depending on the end use of the syngas it might be possible that removal of carbon dioxide is required as well and that an amine unit is the most efficient treating process. In that case the HCN/COS hydrolysis unit will protect the amine system from entering high levels of HCN. It is well documented that high levels of HCN in an amine system lead to corrosion problems and formation of heat stable salts from HCN degradation products (van Grinsven 1999). If an amine system is chosen the SulFerox unit can be used for the treatment of the amine regenerator off-gas.

The optimal flow scheme for syngas treating will be different for each case. However, since Shell Global Solutions' technology portfolio covers the whole range from gasification to HCN/COS hydrolysis to amine treating and sulfur recovery -including the SulFerox process- we are in an unique position to determine the optimal treating scheme.

ALTERNATIVES

One of the major concerns of all liquid redox processes that use $\text{Fe}^{3+}/\text{Fe}^{2+}$ solutions containing ligands to keep the iron in solution at relatively high pH levels -for optimal H_2S removal- is the solvent degradation rate. This degradation of solvent is mainly caused by side reactions occurring during regeneration of the solution with air. This ligand degradation requires the continuous removal of degradation products with the produced sulfur and consequently a continuous addition of chemicals is required. In most cases this is the major operating cost of a SulFerox unit. Over the years a large number of improvements have been made to optimise the regeneration of the solution and to reduce chemicals consumption. Even alternative regeneration (Olson 1984) concepts (electrochemical) and methods to remove by-products from the solution have been explored, however, without changing the fundamental concept of the process.

A new process for the removal of hydrogen sulfide from gases has been developed by Paques Bio System B.V. and Shell Global Solutions (Kijlstra 1999). In this process hydrogen sulfide is removed from the gas phase in an absorber column using a carbonate solution and the conversion of sulfide to sulfur is accomplished by bacteria in a separate bioreactor. Consequently no ligands have to be added to the process (for details of this process see the paper on the Shell-Paques process in session II of this conference). As a result chemicals costs for the Shell-Paques process are generally lower and a number of applications for iron redox technology will in the future inevitably be replaced by the Shell-Paques process. However, even with this new technology in place still a number of applications will be better suited for the SulFerox process including treating of:

1. Gas streams that contain high levels of compounds that are toxic to bacteria.
2. Gases that have an unfavourable $\text{H}_2\text{S}/\text{CO}_2$ ratio.

Since both processes are part of the technology portfolio of Shell Global Solutions an optimal selection of the appropriate H_2S abatement process can always be made.

CONCLUSIONS

The SulFerox process continues to be licensed by Shell International Oil Products B.V. and the authorised licensors Le Gaz Integral and Westfield Engineering & Services. SulFerox chemicals are still being supplied by Dow and supported with solvent analyses.

The trend -observed already two years ago- that the SulFerox process is increasingly applied outside the traditional oil & gas industry continued. Particularly in Europe the abatement of hydrogen sulfide from syngas obtained from the gasification of (municipal) waste is becoming important. Optimal treating schemes taking all the potential syngas impurities into account can be evaluated by Shell Global Solutions.

Efforts to optimise current design and operation of SulFerox units continue. Promising results have been obtained in using alternative sparger designs. Smooth steady state operation can successfully be obtained by automation of the chemicals addition.

Despite emerging new processes the SulFerox process remains competitive for certain applications. The whole range of treating processes that are on the market are in the portfolio of Shell Global Solutions. Consequently an optimal selection of the most suited gas treating process can always be made.

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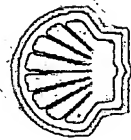
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Shell Global Solutions



PRESENT STATUS SULFEROX PROCESS

by

Cornelis J. Smit and Eva C. Heyman

at

The 9th GRI Sulfur Recovery
Conference

Present status SulFerox process

- Introduction
- Licensing
- Process Developments
 - Optimisation chemicals addition
 - Capital reduction
- Syngas treating
 - HCN/COS
- Alternatives
- Conclusions

Introduction

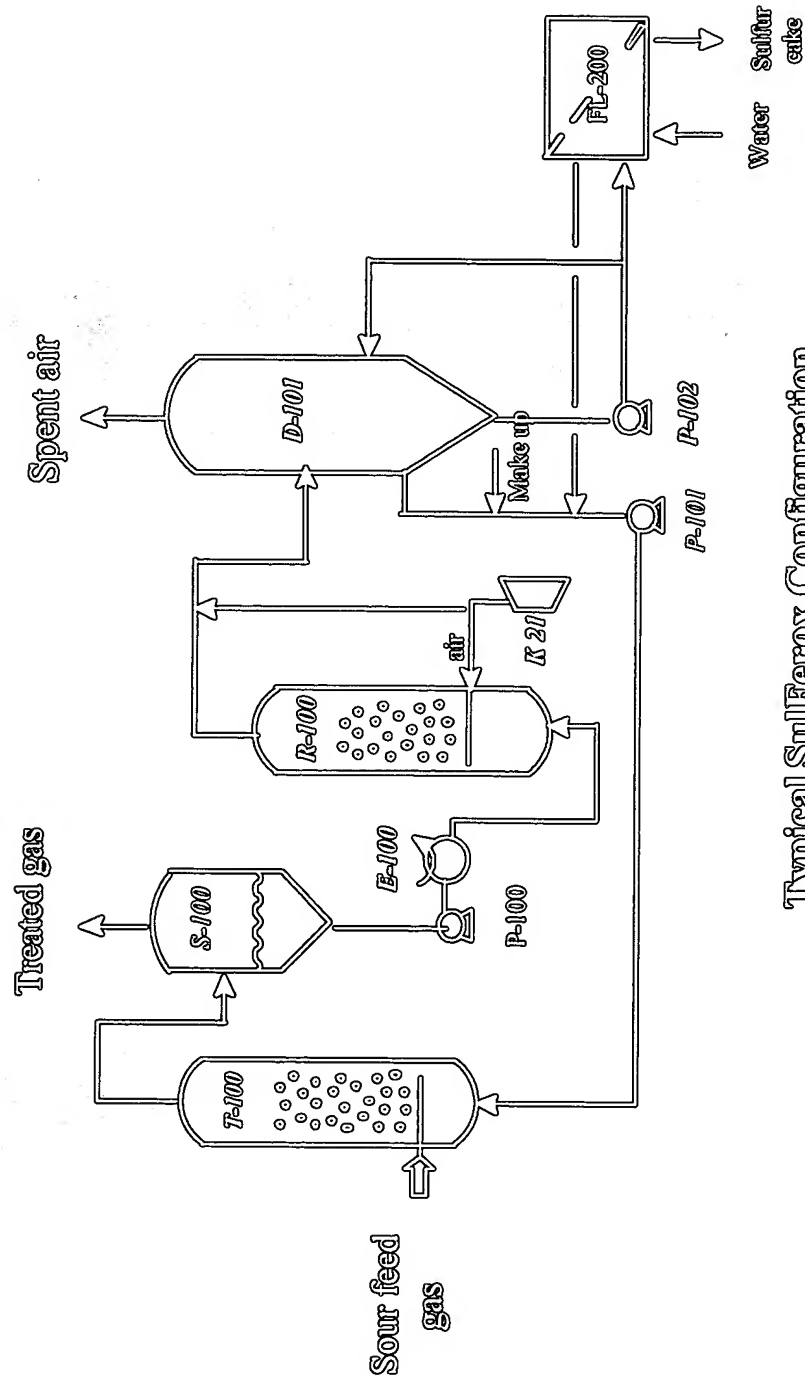
SulFerox main features

Absorber: $2\text{Fe}^{3+}\text{L} + \text{H}_2\text{S} \Rightarrow 2\text{Fe}^{2+}\text{L} + \text{S} + 2\text{H}^+$

Regenerator: $2\text{Fe}^{2+}\text{L} + 1/2\text{O}_2 + 2\text{H}^+ \Rightarrow 2\text{Fe}^{3+}\text{L} + \text{H}_2\text{O}$

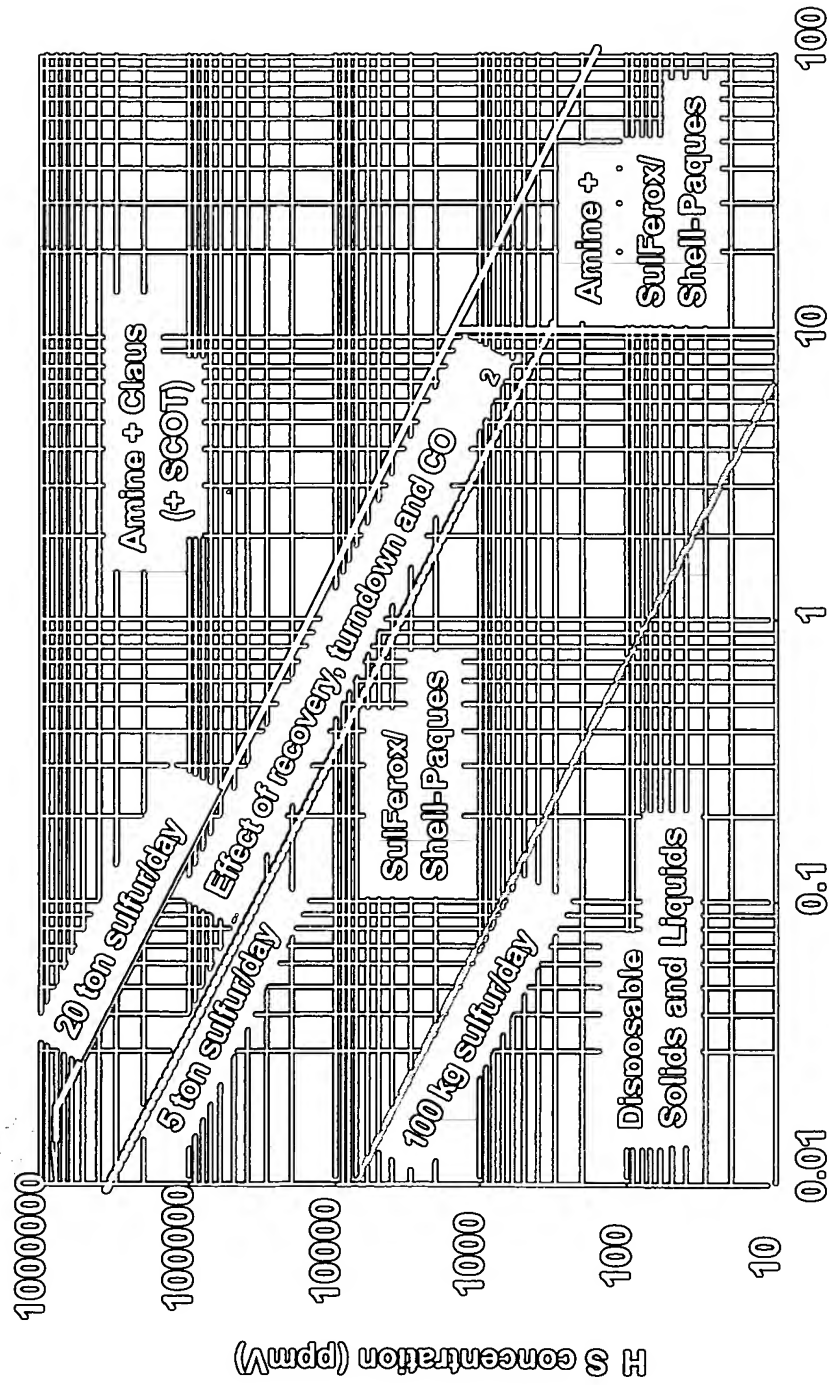
- High iron concentrations; small liquid flows
- Effective absorbers/contactors
- High flexibility and good turndown capabilities
- Consistent operation
- Non toxic sulfur product suitable for agricultural use (depending on local regulations)

Introduction



Typical Sulferox Configuration
Sparged tower contactor

Introduction Applicability of the process



Gas flow (MMNm³/day) multiply by 35.3 for MMSCFD

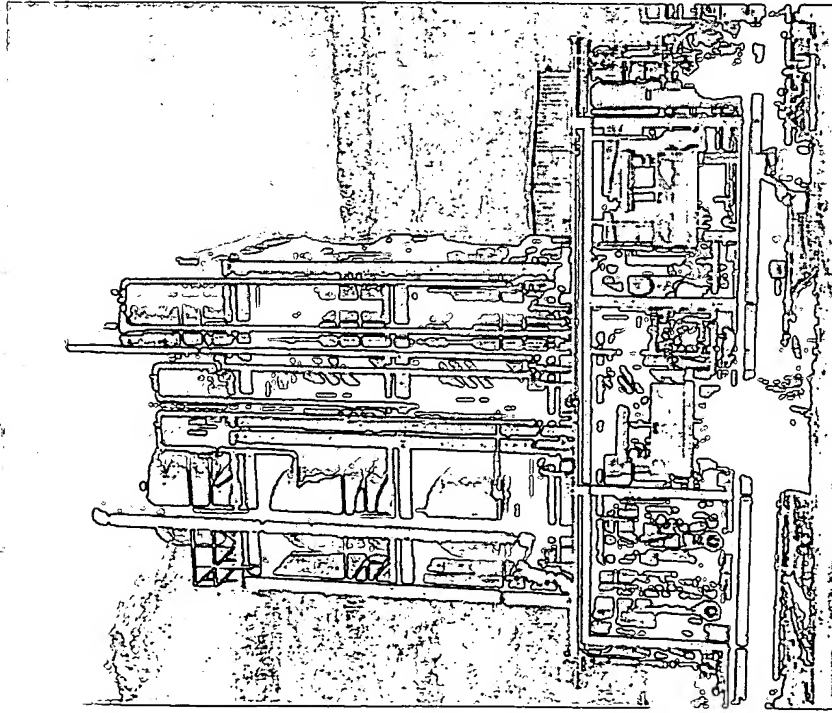
Licensing

- Early 1998 The Dow Chemical Company stopped licensing, but still supplies chemicals
- SHELL continues to license world-wide and authorised licensors are:
 - Westfield Engineering & Services, Houston, USA (in USA)
 - Gaz Integral, Nanterre, France (outside USA)

Process Developments *Optimisation chemicals addition*

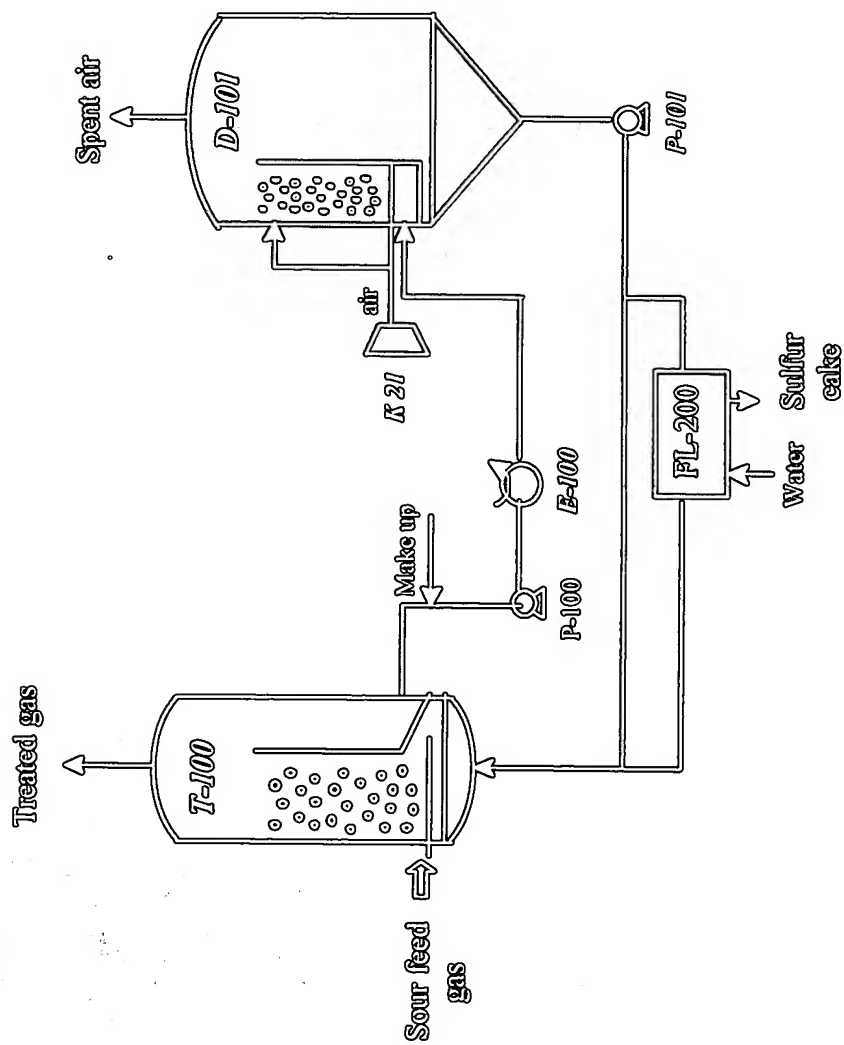
- Variable sulfur production
 - Measure H₂S content on-line
 - Measure flow of sour feedgas
 - Input to computer to control addition pumps and air flow to regenerator
- Advantages
 - More accurate addition of chemicals and regenerator air
 - Saving operator time

Process Developments *Two vessel design*



- Lower Capital Cost
- Smaller Equipments
- Area Requirements
- Reduced Sulfur Plugging
- Easier Maintenance

Process Developments Two vessel design



Typical Two Vessel Sulferox Configuration
Sparged tower contactor/separator

Syngas treating

Sources

- Gasification of coal, oil residues, (chemical) waste and biomass

Issues

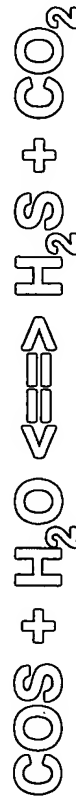
- Reduction of Fe^{3+} by CO/H_2
- Formation of toxic $\text{Fe}(\text{CO})_5$
- HCN/COS present in syngas
 - SulFerox solution quality
 - Total sulfur removal specification

Syngas treating Laboratory testing

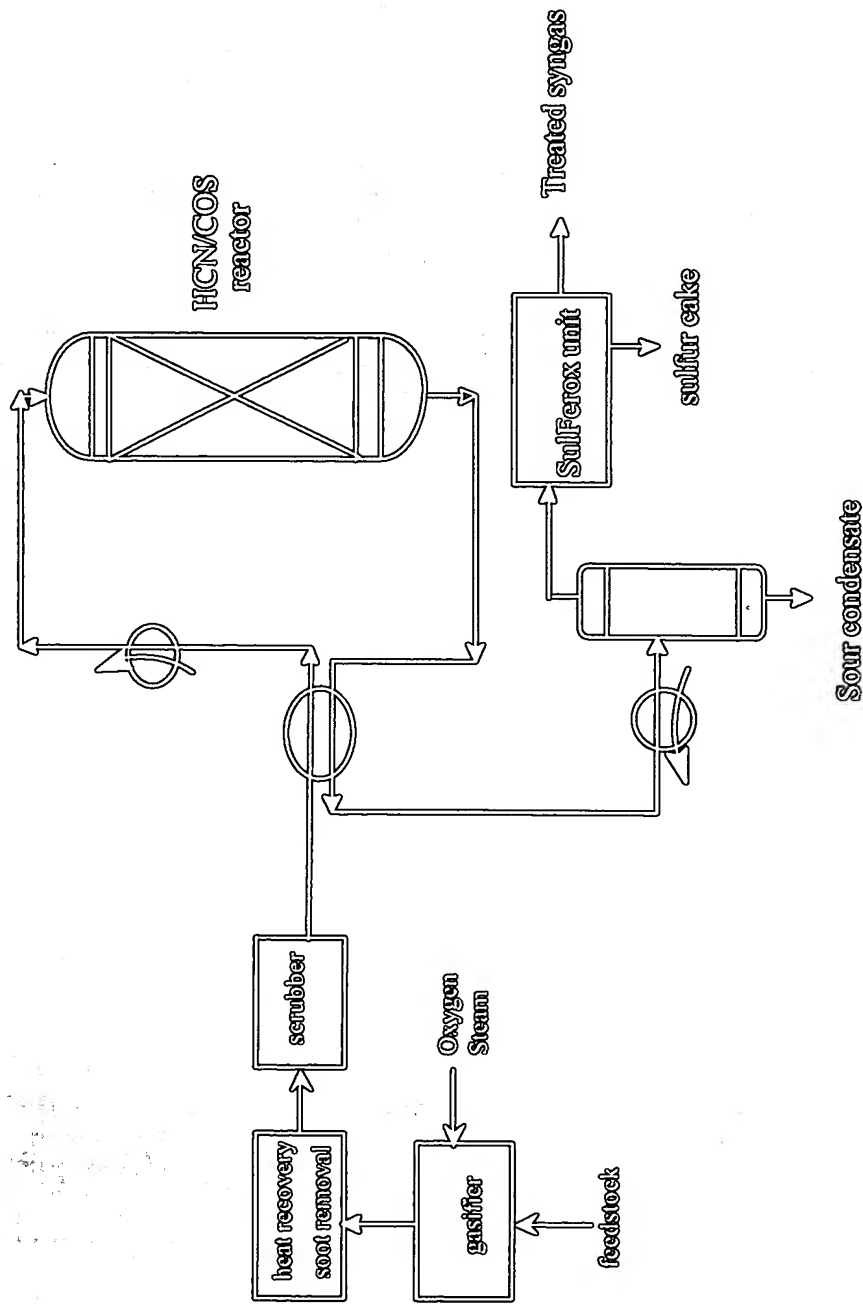
Condition		remarks
Plant pressure psi (bar)	334 (23)	typical for coal gasification
Temperature °F (°C)	104 (40)	
Component	concentration (%V)	
carbon monoxide	60	CO/H ₂ ratio typical for coal gasification
hydrogen	30	
carbon dioxide	1.50	
hydrogen sulfide	0.30	
COS	0.03	in equilibrium with H ₂ S
nitrogen	balance	

Syngas treating Results

- No formation of $\text{Fe}(\text{CO})_5$
- Effective H_2S treat (no Fe^{3+} reduction by syngas)
- HCN/COS hydrolysis required (catalytic)



Generic syngas treating scheme



Generic Syngas Treating Scheme with HCN/COS Hydrolysis and a SulfFerox Unit

Alternatives

- Processes that have lower operating costs (chemicals)
 - Biological processes such as the Shell Paques process (presentation by Paques)
- SulFerox applications in the future
 - Gas streams with unfavourable H_2S/CO_2 ratio
 - Gas streams with compounds that are toxic to bacteria

Conclusions

- SulFerox continues to be licensed by Shell and through Westfield and Gaz Integral
- Developments to reduce capital and operating cost ongoing
- Strong shift from traditional oil & gas industry to syngas and “waste to energy” applications
- Remains to hold a prominent position in gas treating even with emerging technologies

P 203

INDUSTRIAL CHEMISTRY

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